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STAGES OF CERAMIC STRUCTURE FORMATION IN THE PRESENCE OF ADDITIVES

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The effect of various additives on the process of structure formation in ceramics is investigated. The functions of additives at different stages of heat treatment of ceramic mixtures are studied. The possibility of producing articles with prescribed properties is established.

An effective method for controlling the structure and properties of ceramics consists of introducing various additives into ceramic mixture compositions. Such additives include electrolytes, surfactants, water-soluble salts, and various plastifiers. These additives modify the properties of suspensions and plastic mixtures. The burning-out additives to ceramic mixtures include coal, sawdust, lignin, husk, alimentary waste. These additives are used in production of clay brick, light-weight refractories, and other products. Furthermore, various fluxes, mineralizers, slag, and slime are added, which affect the sintering process and the formation of ceramic structure in firing.

The above listed additives can be split into individual and complex additives, depending on their composition, properties, and mechanism of action. The same additive can be attributed to different groups at different stages of the structure-forming process.

A detailed study of the effect of additives at various stages of structure formation makes it possible to determine and justify the choice of the optimum combinations of additives employed to produce articles with high physicotechnical parameters.

The physicochemical process and structural modifications occurring in ceramic mixtures during their preparation and thermal treatment are ultimately reflected in the phase composition, structure, and properties of the obtained material.

V. F. Pavlov and G. N. Maslennikova in [1, 2] investigated in detail the dependences in the "composition – structure – properties" system and proved the possibility of producing articles with prescribed properties. In this context, it is interesting to study the processes and the mechanism of the effect of additives at different stages of ceramic structure formation. We performed numerous experiments in this field.

The analysis of resulting data indicated that the process of structure formation in ceramics can be arbitrarily subdivided into three stages.

The first phase is the formation of a coagulation-thixotropic structure in a ceramic mixture with subsequent transition to a condensation structure. The temperature interval of the first phase ranges from 20 to 120 – 160°C.

The first endothermic effect related to water release is observed on the integrated thermograms of the experimental mixtures within the specified temperature interval. It should be noted that the emerging coagulation structure of the ceramic mixture largely determines the final structure of the produced material.

A uniform distribution of electrolytes, surfactants, and burning-out additives over the ceramic mixture is of great significance at this stage.

Certain additives, in particular, glass cullet, slime, fired kaolin, slag, mineralizers, etc., at the first stage virtually do not react with the main components of the mixture, whereas water-soluble additives actively fulfill their functions. For instance, electrolytes added to the mixtures for ceramic tile production affect the rheological properties of the slip. They liquefy the suspension and, when appropriately chosen, decrease the viscosity and increase the slip fluidity. We used sodium tripolyphosphate as a liquefier in preparing experimental slag-containing mixtures. In addition to that, some other electrolytes were tested, depending on the main mixture components used.

As distinct from mineral electrolytes, which deteriorate the adsorption properties of the components, surfactant particles adsorb on kaolinite particles. In doing so, the main components and moisture are uniformly distributed in the ceramic suspension volume. The uniform distribution of the main components and additives is one of the most important conditions for accomplishing a homogeneous structure in the ceramic suspension and the plastic mixture.

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The process of drying of a ceramic mixture is one of the essential stages in material structure formation. At this stage, simultaneously with moisture removal, the coagulation structure is transformed into a condensation structure. Providing the necessary distribution of moisture in samples and implementation of the optimum drying conditions ensure the possibility of a gradual moisture removal, and this decreases the probability of crack formation in samples and reduces the amount of defects in the course of drying.

Carboxymethyl cellulose (CMC) and microcrystalline cellulose (MCC) introduced as additives to mixtures have a fibrous structure and in drying, as moisture is removed, reinforce the main component particles and improve the sample strength.

The second phase is the transition of the condensation structure of the sample into the crystallization structure. The formation of the solid disperse phase in the ceramic mixture occurs within the temperature interval of 300 – 800°C. Under these temperatures, the presence of additives in the mixture determines the differences in the structural-phase transformation of the components and in the kinetics of the initial sintering phase.

As the temperature in firing ceramic mixtures increases to a level exceeding the limit of existence of condensation structures, complex physicochemical transformations take place. The occurring reactions include polymorphous transformation of β-quartz into α-quartz; reactions of dehydration of argillaceous materials, i.e., kaolinite, hydromica, muscovite, montmorillonite, hydrogoethite, etc.; reactions of decarbonization of calcite and other carbonates of alkali and alkaline-earth metals; burning out of organic additives and impurities.

It can be assumed that the removal of coordinated hydroxyl ions is accompanied by the restructuring of the crystal lattice in argillaceous minerals and the formation of intermediate products.

As a consequence of the thermal destruction of minerals, free oxides arise, which are present in ceramic mixtures in the form of thermally destroyed additives. They, in turn, incorporate in the lattice of metakaolinite and other products of destruction of clay minerals. In doing so, an unstable finely disperse intermediate phase, i.e., a solid solution, is formed.

In the course of crystallizing structure formation in the solid phase, the used additives, depending on their properties, execute the following functions: with increasing temperature, soluble additives are condensed on the argillaceous particles, up to the emergence of condensation-crystallization structures; mineral additives, which disintegrate as a consequence of dehydration and decarbonization reactions, thermally activate the process of the formation of intermediate compounds; and burning-out additives at this stage impart the required porous structure to ceramic materials.

The third phase occurs within the temperature interval between 800 – 900 and 1150°C. At this stage, sintering proceeds with the participation of the liquid phase reacting with the solid phase. The emergence of the eutectic melt at the beginning of this stage determines the new interface boundaries of the disperse phase. The starting temperature of melt formation depends on the mixture compositions and the additives used. For instance, the beginning of liquid phase emergence in mixtures for ceramic tile production correlates with the temperature 750 – 800°C. An addition of alkali metal oxides to a ceramic mixture made of kaolinite clays decreases the temperature of liquid phase formation by 80 – 120°C and shifts the maximum on the viscosity curves toward the lower temperature region. In particular, Li_2O additive decreases the temperature of melt formation and of intense crystallization of mullite (1000°C); whereas on introducing Na_2O and K_2O, mullite formation proceeds intensely at 1100°C. Under higher temperatures, alkali metal oxides facilitate the crystallization of cristobalite.

Additives of oxides of group II metals (CaO, MgO, ZnO, BaO) shift the temperature of the emergence of the melt and the temperature of the first endothermic effect maximum by 50 – 80°C. As is known, the exothermal effects on the thermograms of ceramic mixtures are mainly related to the crystallization of new formations. An addition of magnesium oxide facilitates the emergence of spinellide, cordierite, etc.; an addition of calcium oxide facilitates the formation of helenite, anorthite, and wollastonite. On introduction of alkaline earth oxides to mixtures containing kaolinite clay, the rate of mullite crystallization increases. Alkali metal oxides are usually introduced to ceramic mixtures via pegmatite, nepheline-sienite, perlite, cullet, volcanic rocks, etc. [3].

The oxides of group II metals are introduced via talc, dolomite, magnesite, various slags, slime, and other industrial waste.

We carried out investigations of sintering and structure formation in slag-containing ceramic mixtures. The experiments involved thermophosphogypsum slag containing up to 45 – 55% $CaSiO_3$ (α-wollastonite). The sintering of experimental mixtures was studied under constant heating based on modifications in sample shrinkage and melt viscosity. It was found that thermophosphogypsum slag is an active sintering intensifier which contributes to an early formation of the melt and new crystal phases [4].

The phase transformations in experimental materials were studied using contemporary analysis methods. Their phase composition is represented by α-wollastonite, quartz, amorphous phase, and newly formed crystals of anorthite and β-wollastonite. The formation of anorthite in firing of the slag-containing ceramic mixture occurs both via the diffusion mechanism in the solid phase with the formation of primary fine-crystalline aluminosilicate and via the crystallization of secondary long-prismatic crystals from the saturated solution. The diffusion of calcium and aluminum ions is the basis for the solid-phase reaction between the slag and the amorphous argillaceous residue. The emergence of low-melting eutectic melts facilitates the formation of the melt and intensifies the sintering process. In firing slag-containing

mixtures, the diffusion of calcium ions into clay aluminosilicates and the reciprocal migration of aluminum ions into α-CaSiO$_3$ structure proceed with high intensity. In this case, the equilibrium of the solid-phase reactions is shifted toward the formation of calcium aluminosilicate as the melt viscosity decreases [5].

Concentration of the melt with Ca^{2+} ions accelerates the volume diffusion and the crystallization processes. The formation of calcium aluminosilicates proceeds intensely at 950°C. The slag contained in mixtures contributes to increasing the quantity and decreasing the viscosity of the melt and acts as a mineralizer intensifying the formation of new crystal phases at relatively low temperatures [6, 7].

Analyzing the published data and the results of our studies, one can draw the following conclusions: based on their effect on the ceramic structure formation process, the additives used in production of ceramic materials can be divided into four groups:

– those controlling the properties of suspensions and plastic mixtures;

– those controlling the process of ceramic mixture drying;

– those controlling the sintering process at the stage of solid-phase reactions;

– and those intensifying the process of crystallization of new formations.

The control of the structure and the phase composition of ceramic materials using complex additives makes it possible to produce ceramics with prescribed properties.

In the case of the optimum selection of additives used in ceramics production, it is possible to reduce the product cost by decreasing the consumption of expensive materials and power.

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